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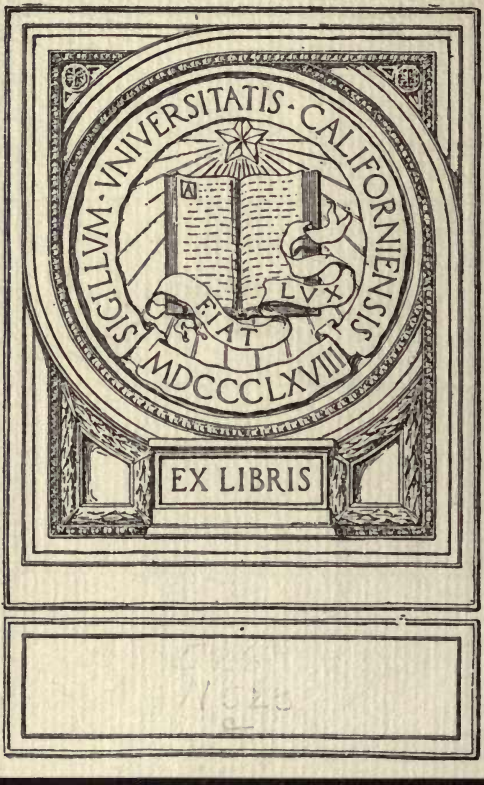
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Catalysis in the Interaction of Carbon with Steam and with Carbon Dioxide

A DISSERTATION

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BY

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Catalysis in the Interaction of Carbon with Steam and with Carbon Iodide

HARVEY ALEXANDER NEVILLE

June 1921

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CATALYSIS IN THE INTERACTION OF CARBON WITH STEAM AND WITH CARBON DIOXIDE.

Introduction.

The interaction of carbon and steam yields, in the first stage of the process, carbon monoxide and hydrogen, according to the equation

$$C + H_2O = CO + H_2.$$

In presence of an excess of steam, and especially with suitable catalytic agents, the primary stage may be succeeded by the following reaction.

$$CO + H_2O = CO_2 + H_2.$$

The first equation represents the desired reaction in the steaming phase of blue water-gas preparation. The second occurs to a certain extent, especially as the temperature of the fuel bed is lowered, the ash content of the coke acting as catalytic agent.[1] In the absence of catalytic agents as, for example, with carbon obtained by the thermal decomposition of hydrocarbons, and therefore ash-free, the first reaction takes place practically exclusively. It is evidently, therefore, a faster reaction than the water-gas reaction in the absence of catalytic agents. The second reaction is the principal reaction in the catalytic process for the manufacture of hydrogen from water-gas and steam. Iron oxide is an important constituent of catalytic agents preferred technically in this process. Since the equation for the water-gas reaction represents an equilibrium which is exothermic in the direction of hydrogen production, it follows that low temperatures and excess of steam favor the elimination of carbon monoxide from the products of the reaction. Temperatures in the neighborhood of 500° are therefore employed in the production of hydrogen by the water-gas catalytic process.

Various attempts have been made to conduct these two reactions in a one-stage technical operation whereby steam is to be passed over carbon of suitable form at a low temperature, so that the reaction products are, in the main, carbon dioxide and hydrogen. To do this efficiently it is necessary to increase the activity of carbon toward steam by the addition of suitable catalytic agents to the reaction mass.

There are a number of patents in existence covering the use of various materials which are to be mixed with charcoal or coke in order to lower the temperature at which the reaction takes place and increase the hydrogen production when the mixture is treated with steam. Among the earliest

[1] Gwosdz, *angew. Chem.*, **31**, 137 (1918).

of these patents is one dated 1867,[2] which proposes the production of hydrogen and carbon dioxide by passing steam over fuel impregnated with lime or caustic soda and heated. Krupp,[3] in a patent of 1892, specifies fuels mixed with hydrates or carbonates. The formation of carbon monoxide is minimized and the carbon dioxide produced is removed by passing over lime. Dieffenbach and Moldenhauer[4] in a series of patents of 1910 suggest the use of coke impregnated or admixed with chlorides, sulfates, or sulfides. Such preparations are stated to be sufficiently active at 600°. With a silicate as catalyst a temperature as high as 750° is used. One of the patents recommends pulverizing the materials, mixing intimately, and briquetting the powdered mixture. It is here claimed that the concentration of carbon monoxide does not exceed a few tenths of 1% when operating at the low temperatures stated. Another patent[5] recommends the admixture of lime in addition to the catalytic agent, in order to absorb the carbon dioxide as it is produced, and thus lower still further the carbon monoxide concentration. A particular preparation mentioned consists of coke impregnated with a 10% potassium carbonate solution and mixed with 5 times its weight of lime, the interval of the reaction temperature being 550–750°. The formation of calcium carbonate is of advantage as the reaction is strongly exothermic and the net thermal effect is therefore positive.

$$C + 2\,H_2O = CO_2 + 2\,H_2 - 19.6 \text{ Kg. Cal.}$$
$$CaO + CO_2 = CaCO_3 + 43.3 \quad \text{“} \quad \text{“}$$

For this reason the duration of steam passage for a given temperature of fuel-bed could be increased.

According to the most recent data,[6] the dissociation pressure of calcium carbonate at 750° is 68 mm. Since the partial pressure of carbon dioxide in the gaseous product would be one-third of an atmosphere, or 253 mm., (assuming the process conducted at atmospheric pressure) if all the steam were converted to hydrogen and carbon dioxide, the lime would, in this case, remove 73% of the carbon dioxide present in the issuing gas. However, there is always an excess of steam, and the partial pressure of carbon dioxide is always less than 253 mm., and hence a smaller percentage is always removed. When the partial pressure of the carbon dioxide falls to 68 mm., none is removed. This will be the case when about 4 times as much steam as will react is being used or, in other words, when a 25% conversion of steam to hydrogen is being obtained. It is thus apparent that the use of lime for the purpose stated cannot be of considerable consequence, unless temperatures in the neighborhood of 550° are used.

[2] Tessie du Motay and Marechal, Brit. pat. 2548, **1867.**

[3] Krupp, Brit. pat. 8426, **1892.**

[4] Dieffenbach and Moldenhauer, Brit. pat. 7718, 7719, 7720, **1910.**

[5] Dieffenbach and Moldenhauer, Brit. pat. 8734, **1910.**

[6] John Johnston, *J. Am. Chem. Soc.*, **32,** 938 (1910).

Since the dissociation pressure of calcium carbonate is only 0.57 mm. at this temperature, a 99% absorption would be attained with a 25% conversion efficiency.

In another list of patents, steam and carbon monoxide, or gases containing it, are passed over coke mixed with metallic oxides and alkalies.[7] Catalysts consiting of metallic couples,[8] such as copper-iron, are also mentioned. Increased pressure is advocated in some cases. For instance, it is stated[9] that, with the use of lime and charcoal, almost pure hydrogen is produced by using steam at ten atmospheres pressure.

Prins,[10] in a patent of 1917, has stated in a more general way the catalysts to be employed in the reaction of steam on carbon. Two or more catalytic agents are to be chosen, one or more from each of the following groups: (*a*) oxygen-containing salts of the alkali or alkaline-earth metals; (*b*) inorganic oxides or hydroxides which behave as non-volatile, weak acids or acid anhydrides, as, for example, boric oxide, aluminum oxide, silicon dioxide. Oxides of iron, chromium, and manganese may also be incorporated, doubtless for the purpose of promoting the water-gas reaction which is the second stage of the process, as was previously pointed out. The specified temperature varies from 300° to 600°. The following mixture, for instance, is stated to be efficient at 400–500°: tricalcium orthophosphate, 1 part; silicon dioxide, 2 parts; coke, 20 parts.

It is apparent that there is in the foregoing statements no information which would indicate the relative merits of the proposed catalysts, the optimum concentration of these, or the effect of temperature change upon the reactions. Neither is there any suggestion of the nature of the mechanism of the catalysis. It was therefore decided in this research to gain some knowledge upon these points by a systematic study of various catalytic agents in their influence upon the reactions. This study has led to a wholly unexpected development of the program of work, since the mechanism of the acceleration by catalytic agents is quite other than was anticipated at the outset.

Many agents were found to catalyze the steam–carbon reaction of which the best were the carbonates of potassium and sodium. With the idea that their influence was to be ascribed to an acceleration of the water-gas reaction, $CO + H_2O = CO_2 + H_2$, this being known to be slower than the steam–carbon reaction in the absence of catalysts; known good catalysts for the water-gas reaction, for example, iron oxide, were tried as catalysts for the steam–carbon reaction. Iron oxide was found to be quite inactive in this respect, and it was evident, therefore, that another explanation of the mechanism must be sought.

[7] Fr. pat. 375164, 459918. Brit. pat. 26770, 1912.

[8] Brit. pat. 6477, 1914.

[9] Ger. pat. 284816. U. S. pat. 1173417.

[10] Prins, Brit. pat. 128273, 1917.

As a possible explanation of the observed catalytic effect in the steam-carbon reaction, it occurred to us that the interaction of carbon dioxide and carbon might be facilitated by the catalytic agents in question and that this was the key to the mechanism of the former reaction. For, if such were the case, the carbon dioxide produced in the second stage of the steaming process, $CO + H_2O = CO_2 + H_2$, would then interact with carbon to form monoxide, $CO_2 + C = 2CO$, which gas, in the presence of the excess of steam, would react as above to form additional quantities of carbon dioxide and hydrogen, thus increasing the net yield of gas from the steam reaction. Experimental tests of this idea showed a complete parallelism between the catalytic effects in the two reactions. In this case reduced nickel was the only catalyst found by us to be superior to the alkali carbonates as accelerating agent, and investigation showed that the low activity of nickel in the steam–carbon reaction was due to a condition brought about by a side reaction, as will be described later. Poor catalysts in the steam-carbon reaction were found to be poor catalysts in the carbon dioxide–carbon reaction, and no material would catalyze this reaction which was not also active in the former case.

As an explanation of the catalytic effect in the carbon dioxide–carbon reaction, it was shown that a mechanism involving alternate reduction and reformation of the alkali carbonates was not correct. These experiments, however, led us to make a determination of the adsorption capacity of carbon for carbon dioxide at the reaction temperatures concerned, both when alone and when impregnated with various catalytic agents. The results of these experiments showed in a striking manner that good catalysts for both of the reactions under investigation also caused a marked increase in the adsorptive capacity of carbon for carbon dioxide as measured at 445°. Our experiments have indicated that this increased adsorption of carbon dioxide by carbon may be attributed to the action of the catalytic agents in facilitating the decomposition of "fixed oxygen" complexes on the carbon surface, thus cleaning the surface to an extent which would ordinarily only be attained by subjecting the carbon to considerably higher temperatures.[11] Definite evidence has also been obtained that such inactive oxygen complexes may be partially broken down into carbon monoxide and carbon dioxide by prolonged heating at the temperature of the experiments, even in absence of catalytic agents, and that they may be reformed by carbon dioxide under these conditions.

II. Experimental.

Materials.—The form of carbon most extensively studied in this investigation was a coconut-shell charcoal produced in large quantities during the recent war for

[11] Lowry and Hulett, *J. Am. Chem. Soc.*, **42**, 1408 (1920).

use in gas masks, and officially known as A909. This charcoal was prepared from coconut shells by carbonization at 950° for 10 hours, followed by steam activation at 950° for 45 minutes.[12] The sample used was passed through an 18-mesh screen and the finer powder removed. The true density of this charcoal was found to be 1.84.[13]

Other forms of carbon used were: (1) sugar charcoal, made by dehydrating recrystallized cane sugar with conc. sulfuric acid, subsequent washing free from acid and heating to dull redness; (2) a high-temperature coke; (3) kelp-char, containing 2.2% of alkali carbonates, calculated as sodium carbonate, which could be extracted with hot water; (4) a retort carbon furnished by the DuPont Company, containing 1.8% of sodium carbonate, determined as above.

The catalysts employed, in the case of salts, were the pure anhydrous compounds. A charge was prepared as follows. The carbon and the catalyst in weighed proportions were moistened with water, mixed thoroughly, and then heated until dry. In this way the catalyst was deposited on the surface and in the pores of the charcoal in a finely divided form, and in intimate contact with the carbon. When reduced nickel was used as catalyst, the desired amount was weighed out as tetrahydrated nickel nitrate ($Ni(NO_3)_2.4H_2O$), dissolved in water and the charcoal moistened with the solution. This mixture was then dried and heated to decompose the nitrate, leaving the oxide of nickel on the surface of the charcoal. The sample was then placed in the reaction tube and reduced *in situ* with hydrogen at the temperature at which it was to be used, that is, 570°. A charge consisted of 8 g. of charcoal plus an amount of the catalyst calculated as a certain percentage of the total weight. For example, A909 plus 20% of potassium carbonate refers to 8 g. of the char mixed with 2 g. of anhydrous potassium carbonate.

Apparatus.—The apparatus used to study the reaction of steam upon carbon was essentially as shown in Fig. 1. It was constructed entirely of Pyrex glass. The internal diameter of the reaction tube was 1.6 cm., and the charge occupied a length of 11 cm. The thermocouple in its sheath was inserted so that its end was at the middle point of the charge. It was made of Hoskins base metal alloys (No. 183 vs. 343; 343 pos.) and was calibrated at several points between 100° and 658°. The temperature was measured by means of a pyrovoltmeter made by the Pyroelectric Company, the accuracy being well within ±5° and the relative variations probably much less. The two joints of the apparatus were made securely gas-tight by wrapping them with rubber dam. The portion of the apparatus extending out of the furnace was wound with resistance wire

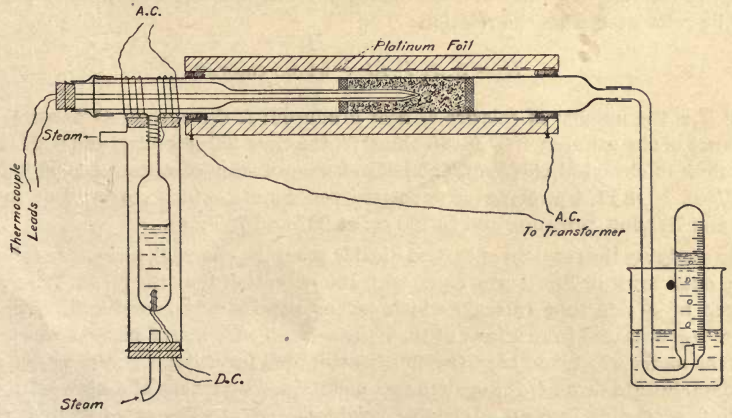

Fig. 1.—Diagram of apparatus.

[12] Lamb, Wilson and Chaney, *J. Ind. Eng. Chem.*, **11**, 420 (1919).

[13] Cude and Hulett, *J. Am. Chem. Soc.*, **42**, 391 (1920).

and heated to prevent condensation of the steam. This steam was generated electrically as shown in the figure. A current of steam was passed through the outer jacket of this generator in order to bring the contents to 100°. Inside, was a platinum spiral of known resistance with leads fused through the glass. This was heated by a constant direct

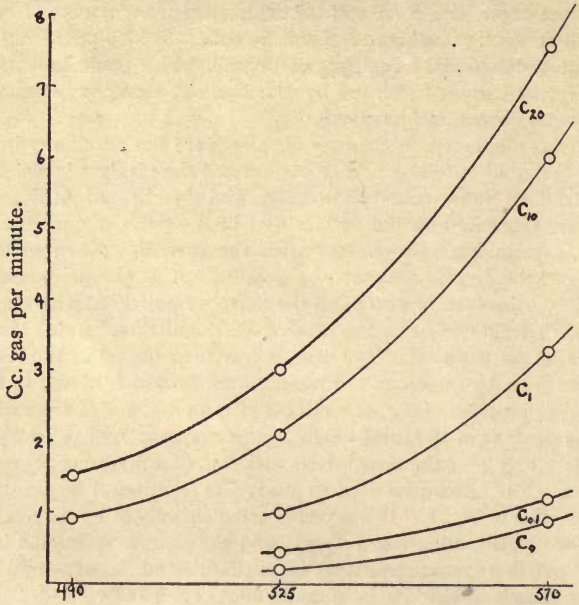

Fig. 2.—Amount of gas produced with different percentages of sodium carbonate.

current to convert the water at 100° to steam. The rate of steam passage per minute could be calculated from the relation

$$H = 0.24\, I^2\, Rt = 64.08 \text{ calories},$$

where H is the number of calories of heat produced; I, the current (1 ampere); R, the resistance of the spiral at 100° (4.45 ohms); t, the time (60 seconds); and 0.24, the heat equivalent of electrical energy. The heat of vaporization of water at 100° is 538 cal.; 64.08/538 = 0.1191 g. of water vaporized per minute, which corresponds to 148 cc. at 0° and 760 mm. pressure, and to 160 cc. at 20° and 760 mm.

In studying the reaction of carbon dioxide upon the charcoal, a reaction tube similar to the one shown in Fig. 1 was used, with the exception that the steam generator was replaced by a side tube through which carbon dioxide was introduced. The carbon dioxide was obtained from a tank of the liquefied gas. Its rate of passage was measured by a flow-meter which had been previously calibrated for this gas. A constant pressure of carbon dioxide through the system was maintained by means of a blow-off through a side tube extending into an adjustable height of water. The gases issuing from this reaction were collected over caustic potash solution in order to absorb the carbon dioxide which had not been reduced. The residual gas was practically pure carbon monoxide, containing a small amount of hydrogen, due either to a trace of moisture in the carbon

dioxide or in the charcoal, or obtained by further decomposition of hydrocarbons not removed from the char in its preparation.

III. Experimental Results.

Steam on Carbon.—The temperatures chosen for this study were conveniently 490°, 525° and 570°. Below 490° the reaction was too slight to be appreciable in most cases, and above 570° the reaction tube softened.

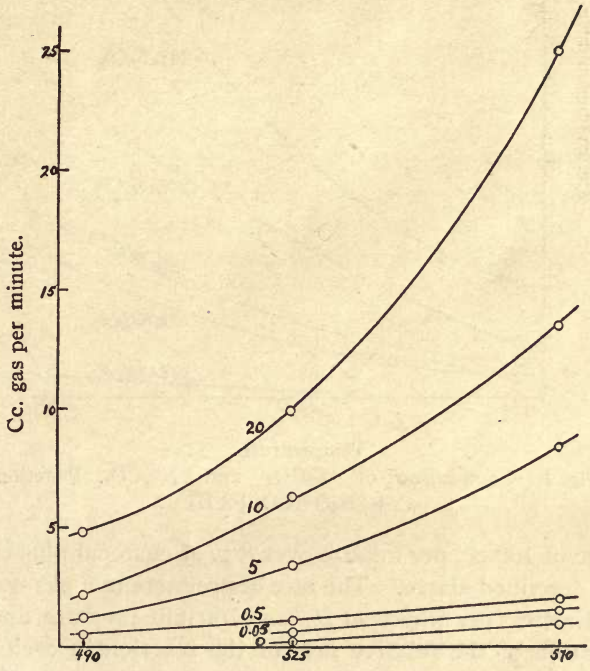

Fig. 3.—Amount of gas produced with different percentages of potassium carbonate.

As a basis for comparison, an experiment was carried out without any catalyst. This was followed by experiments on charcoal moistened with solutions of barium hydroxide, water glass, borax, soda-lime, sodium and potassium carbonates. The last two substances, only, showed a considerable catalytic effect. These two alkali carbonates were subsequently studied as catalysts in detail, in addition to a number of other substances. The results are shown in the accompanying Table I. The data on sodium and potassium carbonates are graphically represented in Figs. 2, 3, 4 and 5. The effect upon the reaction of variations in the temperature and in the amount of catalytic agent employed is clearly indicated in these curves. The results here recorded were obtained by passing steam at a

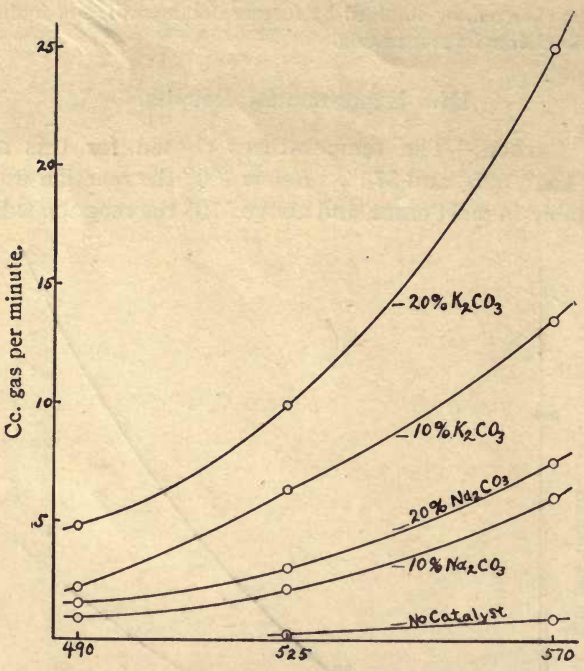

Fig. 4.—Comparison of K_2CO_3 and Na_2CO_3. Reaction $C + 2H_2O = CO_2 + 2H_2$.

constant rate of 160 cc. per minute over 8 g. of charcoal plus the catalyst, prepared as described above. The rate of production of gas was measured in cubic centimeters per minute at 20° and 760 mm. pressure, and was taken as an indication of the relative rate of the reaction in each case. The gases were collected over dil. sulfuric acid and were completely analyzed. Their composition usually approximated a mixture of two volumes of hydrogen and one volume of carbon dioxide, in agreement with the relation $C + 2H_2O = CO_2 + 2H_2$. When there was a deviation from this ratio it could be explained For example, when using lithium, calcium or barium carbonate as catalyst, the proportion of carbon dioxide was too great, owing to dissociation of the carbonate. When an oxidizing agent like sodium nitrate was used, too much carbon dioxide was found in the product because oxidation of the carbon or removal of hydrogen by oxidation had occurred. In this instance, some oxygen also was found.

The presence of carbon monoxide in the reaction product could hardly ever be detected with our gas-analysis apparatus, as the amount present in a 20cc. sample was usually less than 0.05 cc. The theoretical concentration of carbon monoxide at any temperature can be calculated from the water-gas equilibrium, $CO + H_2O \rightleftharpoons CO_2 + H_2$.

At equilibrium,

$$\frac{C_{H_2O} \times C_{CO}}{C_{H_2} \times C_{CO_2}} = K = 0.25 \text{ at } 600°.$$

With steam passing at the rate of 160 cc. per minute, and gas being produced at the rate of 6 cc. per minute, taking into account the fact that $^2/_3$ cc. of steam disappears for every cubic centimeter of gas produced, the equation becomes.

$$\frac{155.3 \times C_{CO}}{4 \times 2} = 0.25.$$

Hence the production of carbon monoxide is at the rate of 0.013 cc. per minute, which represents 0.21% of the gas mixture. When gas is produced at the rate of 25 cc. per minute (cf. A909 + 20% K_2CO_3) the quantity of carbon monoxide becomes 0.24 cc. per minute or 0.96% of the gaseous product.

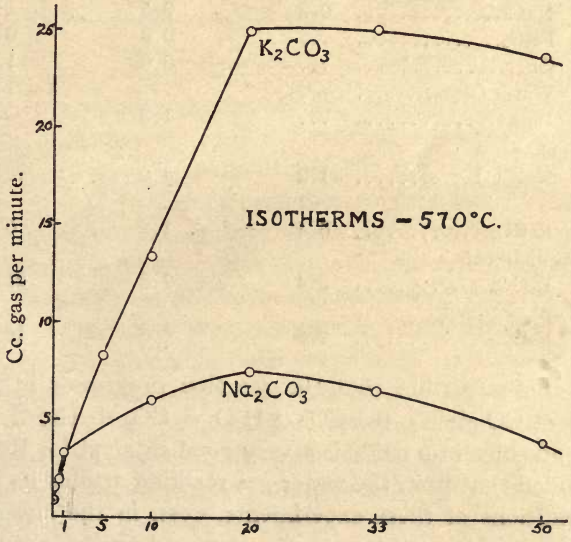

Fig. 5.—Concentration of catalyst in percentages.

The data recorded in Table I make apparent the following facts. (1) Of the materials studied, potassium and sodium carbonates are the only efficient catalysts for the reaction, and potassium carbonate is about three times as active in this respect as the sodium salt. (2) Other salts of the alkalies and alkaline earths have a slight catalytic effect. (3) Iron oxide exerts no influence whatever.

TABLE I.

Material. %	Catalyst.	Cc. gas per minute. At 490°.	At 525°.	At 570°.
A909(8 g.)		0	0.2	0.9
0.05	K_2CO_3	0	0.6	1.5
0.5	K_2CO_3	0.5	1.1	2.0
5	K_2CO_3	1.2	3.4	8.4
10	K_2CO_3	2.2	6.3	13.5
20	K_2CO_3	4.8	9.9	25.0
33	K_2CO_3	4.7	9.3	25.1
50	K_2CO_3	5.0	10.0	23.8
10	Na_2CO_3	0.9	2.1	6.0
20	Na_2CO_3	1.5	3.0	7.5
33	Na_2CO_3	0.7	1.8	6.7
50	Na_2CO_3	...	1.0	4.0
10	K_2CO_3	5.1	10.6	24.0
10	Na_2CO_3			
5	K_2CO_3	2.1		
15	Na_2CO_3		4.9	13.4
20	Li_2CO_3	0.4	1.2	4.1
20	$BaCO_3$	...	0.4	1.3
20	$CaCO_3$	0.2	..	1.1
20	NaCl	0.2	0.5	1.9
10	Fe_2O_3	...	0.3	0.9
20	Cu	...	0.6	1.4
10	Water Glass	...	..	1.0
10	Borax	...	1.3	...
Kelp char				
10	Na_2CO_3	1.2	4.0	18.0
Coke				
20	K_2CO_3	0.4	1.2	5.0
Sugar charcoal				
20	K_2CO_3	3.4	7.5	21.0
DuPont charcoal				
20	K_2CO_3	2.8	6.3	16.8

Since it is almost certain that the reaction progresses in two stages, (a) $C + H_2O = CO + H_2$; (b) $CO + H_2O = CO_2 + H_2$; $C + 2H_2O = CO_2 + 2H_2$, and since iron oxide is a very good catalyst for Reaction b, it may be concluded that first, the water-gas reaction attains its equilibrium under the conditions of these experiments, even in the absence of such substances as iron oxide; and second, the observed catalysis of the reaction between steam and carbon cannot be due to a catalysis of the water-gas reaction but must be due to an acceleration of the first stage or of some other reaction concerned. The catalysis of the reaction, $C + CO_2 = 2CO$, satisfies these conditions and is considered sufficient to account for the increased production of gas when catalytic agents are used in the steam-carbon process.

Charcoal, containing reduced nickel incorporated in the manner previously described, when treated with steam at 570°, produced gas at the

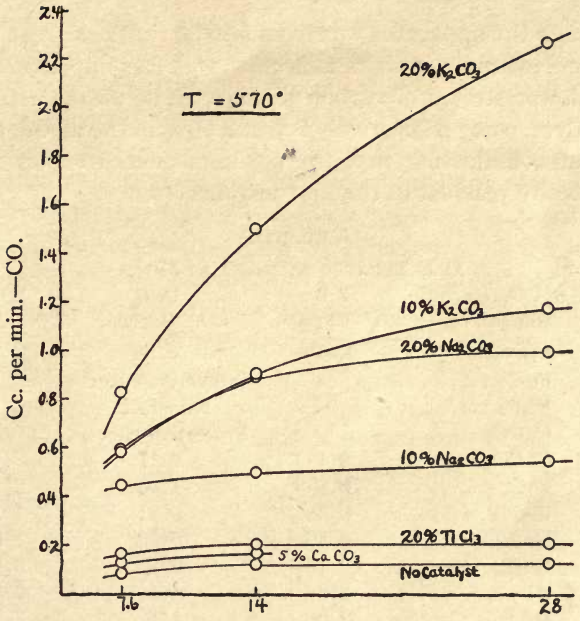

Fig. 6.—Rate of CO_2. Cc. per min.

rate of 80 cc. per minute at the beginning of the operation. After an hour's passage of steam, the rate of evolution of gas had fallen to 6 cc. per minute. It was thought that the decrease in the activity of the nickel as catalyst might be due to surface oxidation by the steam. If this were the case, it should recover its activity when again reduced with hydrogen. The steam generation was stopped and a stream of hydrogen was substituted for it. When steam was again passed through the charge, the evolution of gas was at the rate of 4 cc. per minute, and fell during an hour to an apparently constant value at 2.6 cc. per minute. It is probable that the nickel had either become coated over with a deposit of carbon due to decomposition of carbon monoxide, a reaction catalyzed by nickel, or that it had been agglomerated, by being heated at 570° for a considerable time, into larger particles which had much less catalytic activity.

Carbon Dioxide on Carbon.—Materials similar to those studied in the preceding steam-carbon reaction were used as catalysts for this reaction. The results of these experiments are recorded in Table II and graphically represented in Fig. 6. From a comparison of the values given in the two tables, it is evident that the activities of the catalytic agents are in the same order in the two reactions. These experiments were all carried out at 570°, but the rate of passage of carbon dioxide was varied. An excess of an inactive catalyst such as calcium carbonate mixed with the charcoal produced a more decided protective effect than was observed in the steam-carbon reaction. In the latter case, the velocity of the gas (160 cc. per

minute) through the apparatus was from 5 to 20 times as great and, therefore, the turbulent motion of its molecules was less impaired than in the case of the slower stream of carbon dioxide. The two experiments with nickel as catalyst, using respectively 7.5 and 20% of the metal, gave almost identical results, indicating that the optimun concentration of catalytic agent was already reached in the first instance.

TABLE II.

A909 TREATED WITH CO_2 AT 570°.

Rate of CO_2. Cc./min.		7.6	14.0	28.0
% Catalyst.	Material. A909(8g.)	CO. Cc./min. 0.086	CO. Cc./min. 0.124	CO. Cc./min. 0.137
20	Fe_2O_3.....		Protective effect	
5	Fe_2O_3.....		No effect	
20	$CaCO_3$.....		Protective effect	
5	$CaCO_3$.....	0.133	0.17	..
20	K_2CO_3.....	0.833	1.50	2.27
10	K_2CO_3.....	0.58	0.91	1.18
20	Na_2CO_3.....	0.60	0.92	1.00
20	NaCl.....	0.15	0.20	0.24
7.5	Ni.....	2.3	4.1	7.7
20	Ni.....	2.0	4.1	7.8

The decomposition of carbon monoxide into carbon dioxide and carbon, as was mentioned earlier, was known to be catalyzed by reduced nickel. It was, therefore, to be expected that nickel would catalyze the reverse reaction, $C + CO_2 = 2CO$. Reference to Table II will show that it was by far the best catalyst found. Furthermore, it did not lose its activity as it did in the steam-carbon reaction. The large excess of carbon dioxide in the present instance, no doubt, prevented the reverse reaction from being considerable.

It was supposed by H. St.-Claire Deville, who first observed the decomposition of carbon monoxide, that the decomposition would increase with rise in temperature.[14] However, since the reaction is exothermic, $2\,CO = CO_2 + C + 39$ kg. cal., according to the van't Hoff principle of mobile equilibrium, the quantity of carbon monoxide present in equilibrium with carbon dioxide and carbon will decrease as the temperature is lowered. Boudouard's results[15] for this equilibrium are, 0, 39.0 and 93.4% of carbon monoxide remaining at 445°, 650° and 800° respectively. Rhead and Wheeler[16] found figures substantially in agreement with Boudouard at the higher temperatures by heating carbon in an atmosphere of carbon dioxide, namely 93.77 and 97.78% of carbon monoxide formed at 850° and 900°, respectively. They also noted that the reaction $C + CO_2 = 2\,CO$, proceeded 166 times as fast as the reverse reaction at 850°.

[14] Deville, *Compt. rend.*, **59**, 873 (1889); **60**, 317 (1890).

[15] Boudouard, *ibid.*, **128**, 822, 1522 (1899); *Ann. chim. phys.*, **7**, 24 (1901).

[16] Rhead and Wheeler, *J. Chem. Soc.*, **97**, 2178 (1909).

Following Boudouard's conclusion that carbon monoxide is metastable at 445°, Smits and Wolff undertook to determine the velocity of the decomposition, $2\,CO = CO_2 + C$, in the metastable range, using finely divided nickel as catalyst.[17] They found the reaction to be monomolecular, and assumed that it occurred in two phases: (1) $CO = C + O$, with measurable velocity; and (2) $CO + O = CO_2$ with immeasurably great velocity. They determined that the reaction, in contradiction to the work of Boudouard, was very distinctly reversible at 445°, but found no satisfactory value for the equilibrium constant. The incompleteness of decomposition of carbon monoxide at 445°, as indicated in this research is of importance in reference to the value of 23.15% of carbon monoxide obtained by us in the experiment cited below. These values suggest the necessity of a careful restudy of the equilibrium, $CO_2 + C \rightleftharpoons 2\,CO$, in the interval 445–800°.

Briner and Wroczynski[18] found that, in agreement with the Le Chatelier theorem, the decomposition of carbon monoxide was favored by increased pressure. Rhead and Wheeler corroborate this in a later paper,[19] and apply a formula to calculate the ratio CO/CO_2 at any temperature and pressure:

$$\frac{38055 + 2.02\,T - 0.0031\,T^2}{2\,T} + ln\,P + ln\,\frac{C_1^2}{C_2} = K = 18.75.$$

In the present investigation, when carbon dioxide was passed at a very slow rate over carbon coated with 7.5% reduced nickel at 570°, the resulting gas, collected over mercury and analyzed, was found to contain 23.15% of carbon monoxide. This was the average of 6 analyses which were in close agreement among themselves. As calculated by means of the above formula, the pressure being one atmosphere and, therefore, the middle term dropping out, the concentration of carbon monoxide at 570° should be 17.3%.

Upon the principle that the catalyst for a reaction should also catalyze the reverse reaction, it was attempted to show that potassium carbonate would accelerate the decomposition of carbon monoxide. A stream of carbon monoxide which had been purified and dried was passed at a constant rate of 10 cc. per minute over a charge of charcoal at 570° and the resulting gas was analyzed. The experiment was repeated with the addition of 20% of potassium carbonate to the charcoal. The first analysis showed that 19% of the carbon monoxide had been converted to carbon monoxide and carbon and, in the second case, the decomposition amounted to 29%. A catalytic effect is hereby demonstrated, and evidently the reasoning is orthodox.

[17] Smits and Wolff, *Z. physik. Chem.*, **45**, 199 (1903).

[18] Briner and Wroczynski, *Compt. rend.*, **150**, 1324 (1910).

[19] Rhead and Wheeler, *J. Chem. Soc.*, **99**, 1140 (1911).

Heating Charcoal with the Catalyst.—The idea that the catalysis of the reaction, $C + CO_2 = 2\,CO$, was due to alternate reduction and re-formation of the alkali carbonates was suggested as a possible mechanism of the reaction. This might occur as follows.

$$K_2CO_3 + C = K_2O + 2\,CO,$$
$$K_2O + CO_2 = K_2CO_3.$$

This view was shown to be incorrect by heating some charcoal in an atmosphere of nitrogen, both alone and with 20% of potassium carbonate. The gases evolved during the heating were of the same composition (*ca.* 15% CO and 85% CO_2) in each case, though a somewhat larger amount came off when the catalyst was present. Especially was it true that the gases came off more rapidly when the potassium carbonate was used than when the carbon was heated alone. The gases were presumably due to the decomposition of the surface complex of "fixed oxygen," or C_xO_y, described by Rhead and Wheeler,[20] and recently studied by Lowry and Hulett.[11] These facts seem to indicate that the surface compound may be more readily removed in the presence of substances such as potassium carbonate and that the cleaned surface is then more reactive toward carbon dioxide. If this be true, then the activity of the charcoal alone ought to be much greater after prolonged heating than at first, as a certain amount of the gases is removed finally, even in absence of potassium carbonate. This is correct to some extent, for the reaction of the charcoal with carbon dioxide is considerably greater after a period of heating when no gas is being passed than before, but very soon falls to exactly its original activity after the passage of carbon dioxide has been resumed.[21] These

[20] Rhead and Wheeler, *J. Chem. Soc.*, **103**, 461 (1912).

[21] Effect of heating the char. Eight g. of A909 was heated for 20 hours at 570°. The system was then washed out with CO_2 for 10 minutes.

Passing CO_2 at the rate of 14 cc./min., samples were collected successively.

	Time. Min.	CO produced. Cc.	CO per min. Cc.
(1)	21	13	0.62
(2)	20	8.5	0.425
(3)	35	7.5	0.21
(4)	60	9.5	0.16

Passage of CO_2 was stopped, heating was continued at 570° for 17 hours.

Passing CO_2 again at 14 cc./min. a sample was collected giving

(5)	2.5	20	8.0

The system was washed out with CO_2 for 15 minutes. Samples then collected.

(6)	15	5	0.33
(7)	30	6.5	0.22
(8)	40	7.0	0.17

After three hours with CO_2 passing continuously at 14 cc./min., a sample was taken.

(9)	30	3.7	0.123

This final value agrees with that given in Table II (0.124 cc./min.) obtained by the usual procedure of bringing the charge to 570° in about 2 hours, with CO_2 passing through the system continuously.

results apparently indicate that carbon dioxide is able to reform the surface complex, C_xO_y, or that the gas is adsorbed in some intimate way and changes the reactivity of the carbon.

Rhead and Wheeler state[20] that the oxidation of carbon always consists in the formation of the indefinite oxygen-carbon complex and that this subsequently decomposes into carbon monoxide and carbon dioxide, since both these gases are shown to be primary products in the combustion of carbon. Hence it would appear that the oxidation of carbon by carbon dioxide must take place in some such manner. If carbon can take up carbon dioxide to form C_xO_y, and this complex then decompose to give carbon monoxide and carbon dioxide in a ratio dependent upon the temperature, and if such substances as potassium carbonate can catalyze these reactions, then we have a mechanism which explains the catalysis of the reaction, $C + CO_2 = 2\ CO$, and consequently the catalysis of the reaction, $C + 2\ H_2O = CO_2 + 2\ H_2$.

Adsorption of Carbon Dioxide.—Whether or not a surface oxide is formed and decomposed in the manner indicated cannot be definitely stated. It is, however, certain that the presence in the carbon of such substances as potassium carbonate increases the concentration of carbon dioxide on the surface of the charcoal. This effect is more marked at temperatures higher than those at which adsorption ordinarily plays a part, and this is consistent with the fact that the specific catalytic effect of the same substances increases with temperature. We are inclined to regard such factors as strong presumptive evidence of a $C\text{-}CO_2$ complex formation.

Table III gives a comparison of the catalytic effect of several substances upon the two reactions with their effect upon the adsorptive capacity of charcoal for carbon dioxide. The adsorption measurements were made by means of the apparatus described by Taylor and Burns.[22] The adsorption capacity of reduced nickel for carbon dioxide at 445° was there reported to be negligible. The adsorption on pure potassium carbonate at this temperature was also tested in the present experiments and was found to be practically nil.

TABLE III.

Catalyst. %		Interaction of C and H_2O at 570°. Gas produced. Cc./min.	Interaction of C and CO_2 at 570°. Gas produced. Cc./min.	Adsorption of CO_2 per g. of C. at 445°. Cc.
20	K_2CO_3.....	25	2.3	4.4
20	Na_2CO_3.....	7.5	1.0	2.0
7.5	Ni.....	2.6 (final value)	7.7	1.76
20	NaCl.....	1.8	0.24	0.4
	No Catalyst.....	0.9	0.14	0.33

In the above table the only substance exhibiting anomalous behavior is reduced nickel. Its activity in the carbon dioxide–carbon reaction is above that of the other catalysts, but its effect upon the adsorptive capacity

[22] Taylor and Burns, *J. Am. Chem. Soc.*, **43**, 1273 (1921).

of carbon falls below that of the alkali carbonates. Its irregularity in the steam-carbon reaction was previously noted and discussed; the reason for its loss in activity in that case may also be applicable here.

There is a possibility, in favor of which however no evidence is as yet forthcoming, that steam might also be "fixed" on a carbon surface just as carbon dioxide is; that, moreover, catalytic agents such as potassium carbonate might in such case also bring about an increase in the concentration of steam on the charcoal surface. The experimental method of testing this possibility would not be simple since chemical reaction, to yield hydrogen and carbon monoxide, would occur in part. Furthermore, the technique of adsorption measurements with steam requires extended development before such a viewpoint can be satisfactorily taken.

IV. Summary.

1. The effect of certain catalytic agents upon the interaction of steam and carbon has been studied, using various forms of carbon.

2. It has been discovered that the interaction of carbon dioxide and carbon is likewise accelerated by the presence of the same materials, and a striking parallelism between the catalysts for the two reactions has been demonstrated.

3. The probable mechanism of the steam–carbon reaction has been investigated.

4. It has been shown that good catalysts for the water-gas reaction, for example, iron oxide, are ineffective in the steam–carbon and carbon dioxide–carbon reactions.

5. Catalysis of the water-gas reaction thus being excluded from consideration, it has been shown that the acceleration of the reaction $C + CO_2 = 2\ CO$, and therefore the acceleration of the reaction, $C + 2\ H_2O = CO_2 + 2\ H_2$, may be ascribed to increased adsorption of carbon dioxide by the carbon surfaces in presence of active catalytic agents.

6. Adsorption measurements have been shown to confirm this view.

7. The results obtained have been considered in view of the proposed existence of a surface complex C_xO_y, and have been found to agree with this conception.

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